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ACCELERATION OF THE REACTIVITY OF FLY ASH BY CHEMICAL ACTIVATION

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ABSTRACT:

Experiments were performed to determine the effect of various chemical activators on strength of lime fly–ash pastes manufactured with two types of fly ash — a low calcium subbituminous ash (LFA) and a high calcium subbituminous ash (HFA). The strengths of blends of 80% fly ash and 20% hydrated lime were used to evaluate the pozzolanic reactivity of the ashes. Pastes were continuously moist–cured at 50°C. The results indicate that the addition of small amounts of Na_2SO_4 and $CaCl_2$ can increase the pozzolanic reactivity of both types of ash; this results in a significant improvement in strength. Na_2SO_4 has its predominant influence at early ages; its effect at later ages varies with the nature of fly ash used. In general, early–age strength increases with the amount of Na_2SO_4 dosage. Extent of strength improvement at later ages depends upon the dosage and type of fly ash used. The addition of $CaCl_2$ has a variable influence on strength at early and intermediate ages. However, strengths at 90 days and 180 days are significantly improved by addition of 3–5% $CaCl_2$ activator. The use of up to 5% NaCl rather than $CaCl_2$ did not result in substantial improvements to strength. X–ray analysis suggests that the addition of Na_2SO_4 results in the formation of substantial amounts of ettringite (AFt). Addition of $CaCl_2$ results in the formation of solid solution C_4AH_{13}-$C_3A.CaCl_2.10H_2O$.

Introduction

The quantities of fly ash used in concrete continue to increase due to observations that (a) ash can improve some aspects of the performance of concrete; (b) the use of ash can reduce the cost of concrete, and (c) a consistent quality of ash that produces predictable effects in concrete can be supplied to the producer (1). One clear disadavantage in the use of most fly ashes for cement–replacement purposes is that the replacement of cement, especially in high volumes, decreases rate of early strength development of the concrete.

Research has been performed to examine the effect of some chemical activators on strength of hardened cement pastes manufactured with various blends of fly ash, blast furnace slag, natural pozzolan, calcium

TABLE I
Chemical Composition (% of total mass) and Some Physical Properties of Fly Ashes (3)

	LFA	HFA
SiO_2	57.8	38.1
Al_2O_3	23.0	20.7
Fe_2O_3	3.5	5.2
CaO	9.9	23.9
MgO	1.5	4.6
SO_3	0.3	1.9
Na_2O	2.3	1.4
K_2O	0.5	0.4
Loss on Ignition	0.5	0.4
Glass Content	83.9	64.0
Quartz	4.1	9.0
Mullite	10.2	7.5
Hematite	1.4	0
Density (g/cm^3)	2.0	2.6
Fineness (cm^2/g)	2800	3630
% Passing 45 μm	74	85

hydroxide and Portland cement (2). This paper examines whether significant improvements in the reactivity of fly ash can be realized through the use of some types of chemical activator.

Experimentation

Raw Materials

Two fly ashes were chosen for examination. One is a locally produced subbituminous ash from Alberta that is used extensively in concrete applications throughout Western Canada. The second is a subbituminous ash from Wyoming, U.S.A. Chemical compositions and physical properties are given in Table I, while a comparison of the X-ray diffraction traces for the two ashes is given in Figure 1. The notation used for these ashes is derived from their CaO content — the Alberta ash is denoted LFA as a "low–calcium fly ash", while the Wyoming ash is denoted HFA for "high–calcium fly ash".

A commercial Alberta hydrated lime, commercial flaked $CaCl_2.2H_2O$, reagent grade Na_2SO_4 and purified NaCl were the other chemicals used in the examination.

Preparation and Testing of Specimens

The lime-fly ash cements consisted of 20% hydrated lime and 80% fly ash by mass. The addition of chemical activators are based on the mass of lime-ash cement. The range of addition of activator was 0 – 5%. The water to cement ratio was 0.35 for lime-LFA cement and 0.375 for lime-HFA cement; these values gave approximately constant flows for the two pastes.

Mixing and specimen preparation were performed at room temperature. However, raw materials were heated to make the initial temperature of the fresh pastes approximately equal to the curing temperature of 50°C. The fresh pastes were cast into φ25 glass vials and immediately placed into a saturated limewater bath at 50°C. When the paste cylinders had achieved sufficient strength (usually by one day) they were demoulded quickly and then returned to the bath.

At strength–test ages of 1, 3, 7, 28, 90 and 180 days, four specimens were removed from the bath one hour before the testing time to cool. Ends of the specimens were cut and polished to make the two bearing surface flat and parallel; specimens that were tested for strength had nominal dimensions of φ25 x 50 mm. At each age three specimens were tested for compressive strength; results reported are averages of three tests. The maximum coefficient of variation of strength results was 8%.

After the strength tests pieces of specimens were ground to a powder in 2-propanol then vacuum-dried at ambient temperature in a desiccator until constant weight. The powders were kept in sealed containers

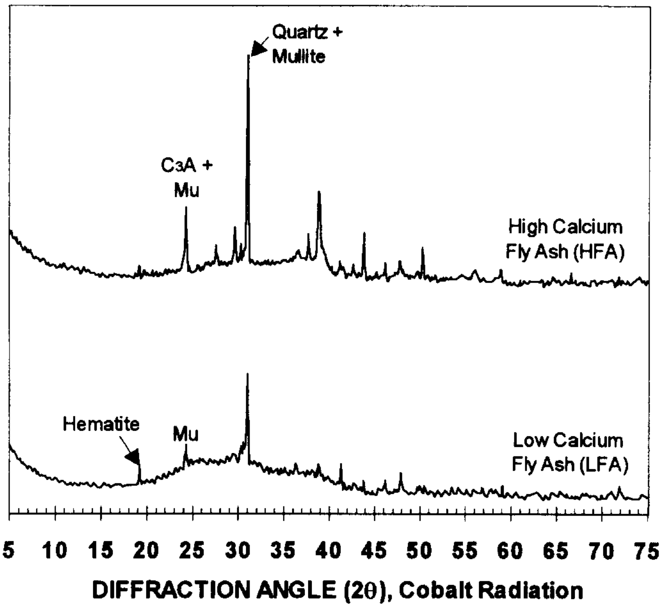

FIGURE 1

X-Ray Diffraction Patterns for the Fly Ashes

until X-ray diffraction tests were performed. A Philips X-ray diffractometer was used to identify the hydration products.

At each age the 4th cylinder was cut into small fragments and placed in a bath of pentane at -125°C. After 2-3 minutes in the bath, these fragments were freeze-dried for 24 hours to remove all free water and then stored in sealed containers; the procedure has been outlined previously by Orr (4). The fragments were were used for the observation of morphology of hydration products by scanning electron microsope.

Results And Discussion

Fig.2 is a summary of the strength results for both sodium sulphate and calcium chloride activation. For brevity of discussion below, the lime-LFA pastes and the lime-HFA pastes will simply be denoted LFA and HFA pastes respectively.

Effect of Na_2SO_4 Dosage on Strength Development of Lime-fly Ash Cement Pastes

Figure 2(a) shows the effect of various additions of sodium sulphate on strength development. At 1 and 3 days, the increase in strength of the LFA pastes with Na_2SO_4 dosage is approximately linear. Beyond 3 days the addition of 1 or 2% Na_2SO_4 does not appear to benefit strength development. Note that the reduction in strength at 180 days for 1% addition is not statistically significant (5% level). There is, however, a clearly significant improvement of strength at 90 days and 180 days for Na_2SO_4 activator dosage in the range 3 to 5%.

The effect of Na_2SO_4 dosage on the strength of HFA pastes is somewhat different than that of the LFA pastes — right side of Fig.2(a). Up to 90 days there is a clear increase in strength over all dosage levels, when compared to the control (0%) paste. The large increase in 1-day strengths is particularly significant. In large-volume concrete applications it can be expected that internal temperatures will rise well

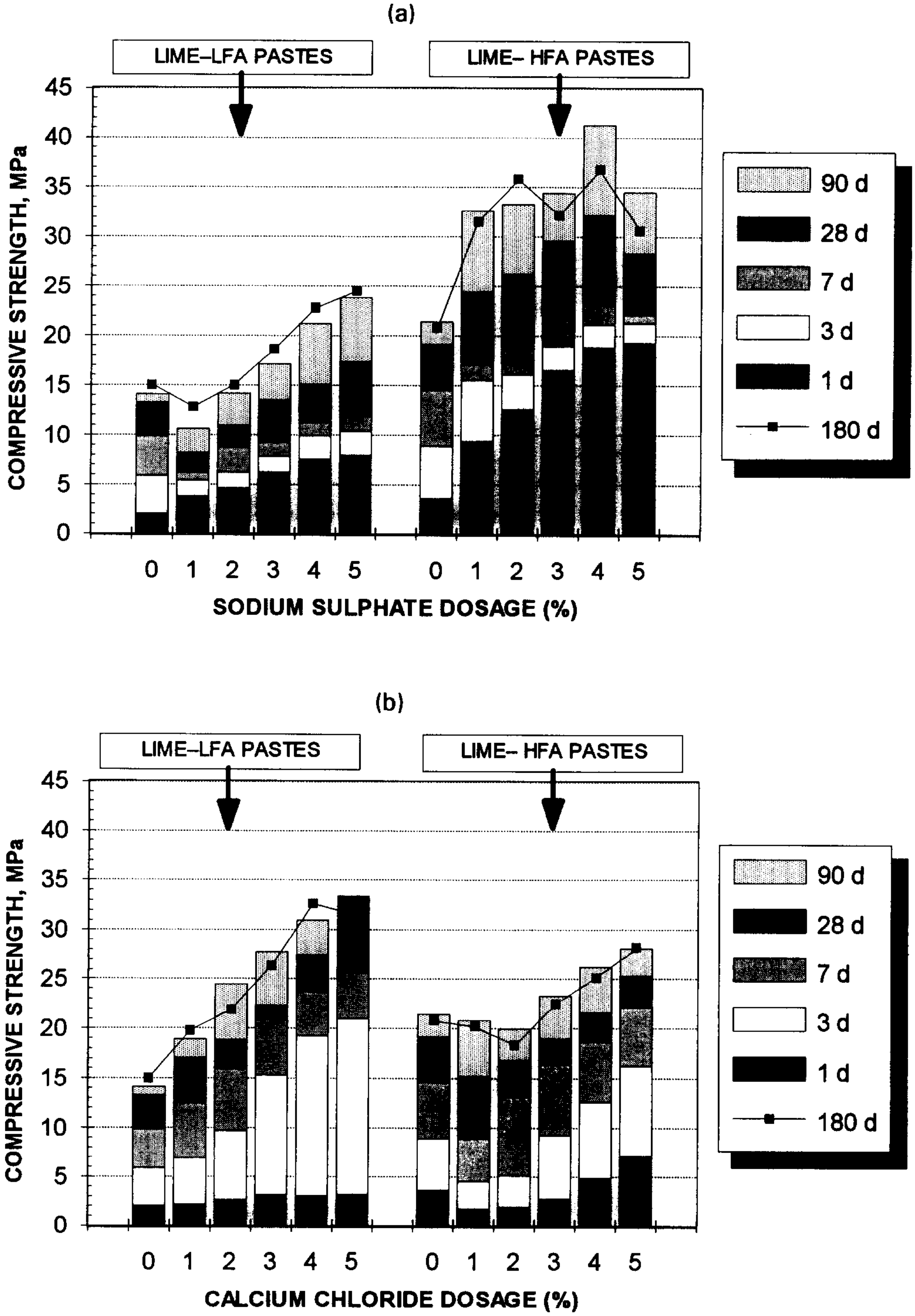

FIGURE 2

Effect of Sodium Sulphate and Calcium Chloride Activators on Strength above ambient for the first few days; the presence of sodium sulphate activator in such an environment is likely to have an appreciable effect on the rate of activation of fly ash, and thus on the rate of strength development of the concrete at early ages. One must keep in mind, however, that there are other factors besides strength which may be influenced by the presence of significant amounts of sodium sulphate — possibly to the detriment of the quality of the concrete.

The addition of Na_2SO_4 has a larger influence on HFA pastes than on LFA pastes. This may be attributed to the higher propotion of reactive aluminates in HFA than that in LFA. This is discussed in more detail below. Although the apparent regression in strength between 90 days and 180 days for some of the HFA pastes is not, on average, statistically significant, more tests need to be performed to examine whether sodium sulphate may have a detrimental effect on long term properties.

Effect of $CaCl_2$ Dosage on Strength Development of Lime-Fly Ash Cement Pastes

The effect of $CaCl_2$ dosage on strength development of LFA and HFA pastes is shown in Fig.2(b). For both types of paste the addition of calcium chloride has no significant effect on 1–day strength [this effect is similar to that observed for lime–natural pozzolan pastes (5)]. After 1 day, however, the strength of LFA pastes is improved substantially by dosages of calcium chloride from 1 to 5%. For HFA pastes this improvement is only significant for dosages in the range 3 to 5%.

Note the interesting contrast between the effect of sodium sulphate and the effect of calcium chloride on the two types of paste. Sodium sulphate has the more pronounced improvement on HFA pastes, while calcium chloride benefits LFA pastes more than HFA pastes. For maximum benefits one clearly must match the type of activator with the type of material being activated.

It was found during the casting of specimens that the addition of Na_2SO_4 retards setting while $CaCl_2$ accelerates the setting of HFA pastes. The higher the dosage, the more conspicuous was the acceleration or retardation effect.

Effect of NaCl on Strength Development of Lime-HFA Pastes

Figure 3 shows the strength development of HFA pastes with NaCl dosages from 0 to 5%. No significant effect of NaCl is observed. This same observation was made when pastes made from natural pozzolan and lime were tested (2). Although no tests were performed with NaCl on LFA pastes, it can be deduced that the same lack of activation of NaCl would be observed, since the chemical composition of the low calcium fly ash is very similar to the composition of the natural pozzolans that were tested.

Effect of Activators on Hydration Products

The sensitivity of the two fly ashes to the type of activator arises because of differences in the chemistry and mineralogy of the ashes. X-ray diffractometry (XRD) and scannning electron microscopy (SEM) were used to examine pastes with and without activators. Although no quantitative X-ray diffraction was performed it is believed that observations of consistent trends in changes of peak intensities, combined with SEM observations, can lead to reliable hypotheses concerning mechanisms of activation.

Hydration Products in Pastes Without Activator: Table II summarizes conclusions concerning the hydration compounds present in the two lime-fly ash pastes without activators. One principal hydration product of both pastes is C–S–H. Other products of hydration depend specifically upon the chemistry and mineralogy of the ash. The second major product in LFA pastes is C_4AH_{13}. For HFA pastes C_4AH_{13} is present at early ages, but at all ages C_3AH_6 appears to be a major hydration compound. The minor products in the two pastes are also different: ettringite (AFt) peaks appear at early ages and C_2ASH_8 forms

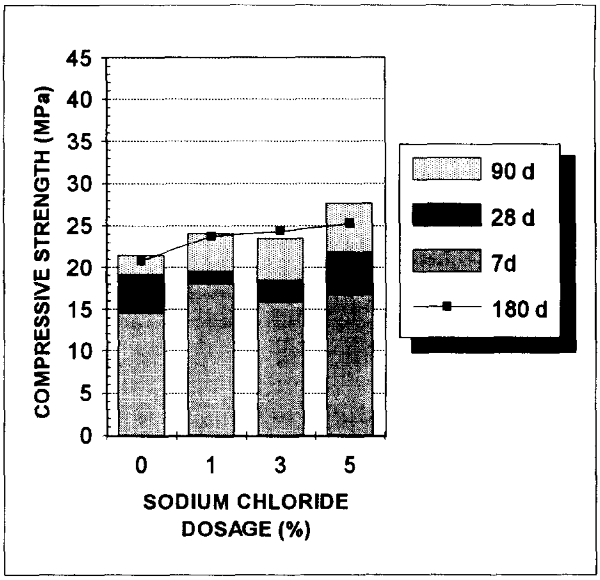

FIGURE 3

Influence of Sodium Chloride Activator on Strength Development

at later ages in the LFA pastes. For the HFA pastes, monosulphoaluminate (AFm) was identified up to an age of 7 days, while no other minor products were detected at 28 and 90 days.

Effect of Sodium Sulphate Activator: At 1 day in the Na_2SO_4—LFA pastes, the diffraction intensity of the AFt major peak increases with activator dosage. Conversely, at one day the diffraction intensity of C_4AH_{13} decreases with dosage up to 3% and C_4AH_{13} peaks were not observed in pastes with activator dosage in the range 3–5%.

For LFA pastes at 7 days and thereafter, AFm rather than AFt was detected at 1 or 2% Na_2SO_4 dosages, while above 2% dosage. Only AFt was detected. Detection of AFm by X-ray analysis was accompanied by SEM observations of hexagonal plates dispersed throughout the microstructure. It was observed that at 1 day the peak intensities of AFt in LFA pastes increase with the dosage of Na_2SO_4. At the same time strength increases almost linearly with dosage. Although no causal relationship can be confirmed, it is postulated that a significant increase in ettringite content at 1 day due to activator dosage has a key influence on the observed compressive strength.

TABLE II

Hydration Products of LFA and HFA Pastes without Activator. Cure at 50°C. Check mark indicates identification of compound

	Age (d)	CSH	C_4AH_{13}	C_3AH_6	AFt	AFm	C_2ASH_8
LFA	1	☑	☑		☑		
	7	☑	☑				☑
	28	☑	☑				☑
	90	☑	☑				☑
HFA	1	☑	☑	☑		☑	
	7	☑	☑	☑		☑	
	28	☑		☑			
	90	☑		☑			

In HFA pastes, the addition of Na_2SO_4 appears to accelerate the formation of one of the main hydration products of this type of ash — C_3AH_6. Although the addition of different amounts of Na_2SO_4 results in the formation and transformation of AFt (similar to the LFA pastes), it seems that the influence of C_3AH_6 dominates the strength development of the pastes. Thus, the strength of lime-HFA pastes continues to increase with Na_2SO_4 dosage at later ages.

Effect of Calcium Chloride Activator: In LFA–$CaCl_2$ pastes, the intensity of diffraction peaks for C_4AH_{13} was seen to increase significantly with $CaCl_2$ dosage. Also, as calcium chloride dosage increased, the main diffraction peak for C_4AH_{13} shifted from 7.89 to 7.74 Å. This shift is believed to be associated with the formation of a solid solution of C_4AH_{13}-$C_3A.CaCl_2.10H_2O$. It is postulated that the formation of this compound reinforces and strengthens the paste; thus, the strengths of LFA pastes increase as $CaCl_2$ dosage increases.

The addition of $CaCl_2$ to HFA pastes results in a reduction in the amount of C_3AH_6 formed — as evidenced by a pronounced reduction in the intensity of the corresponding X-ray diffraction peaks. However, as $CaCl_2$ dosage increases, the amount of solid solution of C_4AH_{13}-$C_3A.CaCl_2.10H_2O$ also increases. The interaction of these two mechanisms may be responsible for the small reduction in strength followed by an increased strength at $CaCl_2$ dosage increases [Fig 2.b].

Conclusions

The conclusions noted below are based upon the research performed on lime–pozzolan pastes made from two subbituminous fly ashes and cured in water at 50°C.

Lime–ash pastes made from two types of fly ash show different types of hydration product and show different degrees of sensitivity to chemical activator. Differences in performance are due to differences in the chemistry and mineralogy of the two subbituminous ashes examined.

Chemical activators can significantly improve the rate of strength gain, and especially early rate of strength gain, associated with the reactivity of fly ash. For the two fly ashes and three activators examined, the use of $CaCl_2$ activator produced the highest strengths in the pastes with low calcium ash (LFA). For pastes made with high calcium ash, Na_2SO_4 was the more efficient activator.

The influence of a particular activator on the strength of lime–ash pastes appears to be primarily due to specific influences that the activator has on the quantity and types of hydration products.

Acknowledgement

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